Tensile stress and creep in thermally grown oxides

Scientific Achievement

We have found that large tensile stresses spontaneously develops in α -Al₂O₃ that is thermally grown on a Fe-Cr-Al(Y) alloy. The tensile stress develops as the early oxide, an Fe and Cr-rich mixed sesquioxide, (Fe,Cr,Al)₂O₃, converts to α -Al₂O₃ during the growth process. A lattice parameter contraction, which accompanies the composition change, leads to a tensile stress in the constrained oxide. We also show that the stress is relaxed by creep in the oxide.

The occurrence of growth stresses in thermally grown oxides (TGO), and mechanisms which cause them, are poorly understood. Especially controversial is the possibility that tensile stresses develop during isothermal growth conditions. In recent x-ray diffraction (XRD) studies, Tortorelli, et. al. *Mater. at High Temp*, **20**, 303 (2003), reported that very large tensile stresses, close to 1 GPa, developed in the alumina TGO formed on a Fe-Cr-Al(Y) alloy. The mechanism for this surprising result was not identified. We have confirmed the Tortorelli result and have identified the mechanism driving this behavior.

This tensile stress generation mechanism has not previously been recognized in alumina formers, even though it must play an important role in the formation of protective oxides on a wide range of commercial structural alloys. The identification of this growth mechanism provides a significant advance in the field of oxidation; prior reports of tensile growth stresses have generally been regarded as highly controversial.

This work has been accepted for publication in *Nature Materials*.

Significance

Information about the role of growth strains is needed for guidance in developing improved protective oxides and for modeling protective oxide behavior for in-service applications. Structural components that operate at high temperatures (e.g., turbine blades) rely on a thermally grown oxide, commonly alumina, for corrosion protection. Knowledge of strain evolution in the TGO during the growth process and during thermal excursions is needed to obtain improved understanding of growth and failure mechanisms. A new capability, exploiting in-situ measurements using synchrotron radiation, was developed for these experiments. Providing unprecedented accuracy and precision, the new technique is revealing the oxide growth processes that lead to high levels of strain generation

The separation of competing oxide growth mechanisms which result in strain generation or relaxation will require considerable effort. As dominant growth mechanisms are identified and quantified, the more subtle competing mechanisms can be isolated and studied.

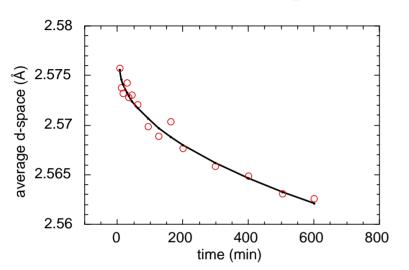
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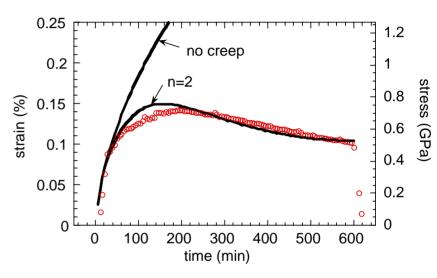
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Tensile stress and creep in thermally grown oxides (TGO)

- A large tensile stress is observed in α -A₂O₃ isothermally grown of Fe-Cr-Al-Y alloy
- This work confirms controversial result (Tortorelli, et. al., ORNL). Mechanism is explained
- Role of stresses in TGO is important for high temperature materials but poorly understood





Left panel: Average d-space of (104) diffraction ring contracts as composition of the growing oxide changes from $(Fe,Cr,Al)_2O_3$ to α -Al₂O₃.

Right panel: Lattice parameter contraction in the constrained oxide leads to a tensile stress as growth proceeds. Open circles: measured strain. Upper curve: Strain calculated from change in d-spacing (no creep is considered). Lower curve (exponent n = 2): creep is included.

